Condensed Thiophen Ring Systems. Part XIV.[1,2] Photolysis of Azidobenzo[*b*]thiophens in Secondary Amines

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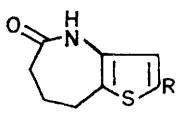
Photolysis of 4-azidobenzo[*b*]thiophen in diethylamine gave a mixture of starting material, 4-aminobenzo[*b*]thiophen, 4,4'-azobenzo[*b*]thiophen (5), tar, and a trace of an unidentified compound. In contrast, 5-azidobenzo[*b*]thiophen gave 4-amino-5-diethylaminobenzo[*b*]thiophen (6) as the only isolable product. The 4-amino-5-dialkylaminobenzo[*b*]thiophens (7)—(9) were prepared similarly by photolysis of a 5-azidobenzo[*b*]thiophen in the appropriate secondary amine. The mechanism of formation of these products is discussed. Ethyl 5-azidobenzo[*b*]thiophen-2-carboxylate was photolysed and thermolysed in various other nucleophilic solvents to give products derived from a triplet nitrene only. Ethyl 4-amino-5-diethylaminobenzo[*b*]thiophen-2-carboxylate was converted into ethyl 3-ethyl-2-methylthieno[3,2-*e*]benzimidazole-7-carboxylate with a mixture of formic acid and hydrogen peroxide.

In connection with other work we were interested in thienoazepines, a relatively unexplored class of compounds. The 4,6,7,8-tetrahydrothieno[3,2-*b*]azepin-5-ones (1; R = H, Me, or halogen) and the isomeric 5,6,7,8-tetrahydrothieno[3,2-*c*]azepin-4-ones (2; R = H, Me, or halogen) may be prepared from the corresponding 6,7-dihydrobenzo[*b*]thiophen-4(5*H*)-ones (3) by means of a Beckmann [3a-c] or a Schmidt [3b,4] reaction. The parent compound (2; R = H) undergoes bromination to give the 2-bromo-derivative (2; R = Br), which is nitrated in the 3-position.[4] Similar reactions have been reported for the parent system (1; R = H).[3c,d] The 4*H*-thieno[3,4-*d*]azepines (4; R^1 = H, Me, or Cl, R^2 = H or Br) may be prepared through cyclisation of 3,4-bis(cyanomethyl)thiophens in acid.[5]



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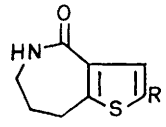

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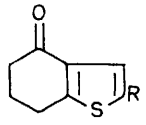

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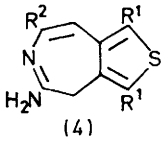

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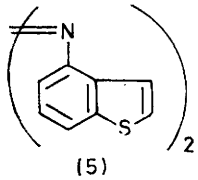

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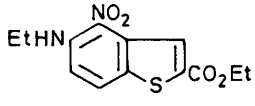

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In an attempt to synthesise thienoazepines by a reaction analogous to the photolytic ring-expansion of aryl azides to azepines in amines [6] we irradiated 4-azidobenzo[*b*]thiophen in a large excess of diethylamine for 18 h. Apart from starting material (40% recovery), this gave 4-aminobenzo[*b*]thiophen (59%),† 4,4'-azobenzo[*b*]thiophen (5) (20%), tar, and a trace of an unidentified compound. These products are analogous to those obtained by similar treatment of azidonaphthalenes [7,8] and suggest the intermediacy of a triplet nitrene.

In contrast, 5-azidobenzo[*b*]thiophen gave 4-amino-5-diethylaminobenzo[*b*]thiophen (6) (24%), together with an intractable tar, on photolysis for 18 h in a large excess of diethylamine. Photolysis in morpholine gave the diamine (7) (40%), and the diamines (8) (57%) and (9) (24%) were obtained when ethyl 5-azidobenzo[*b*]thiophen-2-carboxylate was photolysed in diethylamine or piperidine, respectively.

Although the spectroscopic properties of the diamines were as expected, they did not allow us to differentiate between the assigned structures (6)—(9) and those of the isomeric 5-amino-4-dialkylaminobenzo[*b*]thiophens. We were able to distinguish between the possible structures by use of the nuclear Overhauser effect, as follows. Irradiation at the frequency of the amino-protons (τ 5·30) in the n.m.r. spectrum of compound (8) resulted in a 12% increase in intensity of the signal assigned to the 3-proton (τ 1·87), while the signal of the 6-proton was unaffected. Irradiation at the frequencies of the methyl or methylene protons did not affect the signals of the 3- and 6-protons. These results agree with structure (8). Moreover, deamination of this diamine *via* a diazonium compound gave a product with the spectroscopic properties expected for ethyl 5-diethylaminobenzo[*b*]thiophen-2-carboxylate. Compounds (6) and (8) readily formed diacetyl derivatives.

An attempt to synthesise the diamine (8) through nitration of ethyl 5-acetamidobenzo[*b*]thiophen-2-carboxylate, hydrolysis of the resulting 4-nitro-derivative,

† Yields cited are based on starting material consumed.

[1] Part XIII, B. Iddon, H. Suschitzky, and D. S. Taylor, preceding paper.

[2] Preliminary communication: B. Iddon, H. Suschitzky, and D. S. Taylor, *J.C.S. Chem. Comm.*, 1972, 879; presented at The Chemical Society Annual Meeting (Heterocyclic Section), Manchester, 10—14th April 1972, abstract no. 9.9.

[3] B. P. Fabrichnyi, I. F. Shalavina, and Ya. L. Gol'dfarb (*a*) *J. Gen. Chem.* (*U.S.S.S.R.*), 1961, **31**, 1152; (*b*) *J. Org. Chem.* (*U.S.S.R.*), 1965, **1**, 1526; (*c*) 1969, **5**, 346; (*d*) *Doklady Akad. Nauk. S.S.S.R.*, 1965, **162**, 120 (*Chem. Abs.*, 1965, **63**, 11,538).

[4] S. Nishimura, M. Nakamura, M. Suzuki, and E. Imoto, *Nippon Kagaku Zasshi*, 1962, **83**, 343 (*Chem. Abs.*, 1963, **59**, 3862).

[5] C. Hoogzand, J. Nielsen, and E. H. Braye, *Chem. Comm.*, 1971, 1520.

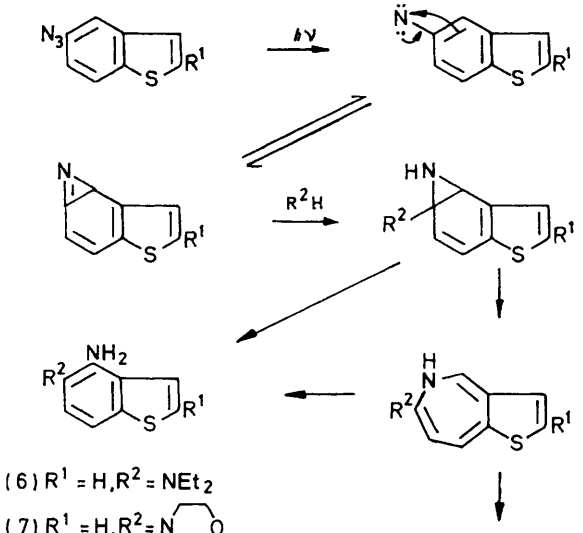
[6] R. J. Sundberg, S. R. Suter, and M. Brenner, *J. Amer. Chem. Soc.*, 1972, **94**, 513, and references cited therein.

[7] R. Selvarajan and J. H. Boyer, *J. Org. Chem.*, 1971, **36**, 3464.

[8] R. Huisgen, D. Vossius, and M. Appl, *Chem. Ber.*, 1958, **91**, 1; R. Huisgen and M. Appl, *ibid.*, p. 12.

and alkylation of the ethyl 5-amino-4-nitrobenzo[*b*]thiophen-2-carboxylate produced with ethyl iodide gave only a low yield of the monoalkyl derivative (10).

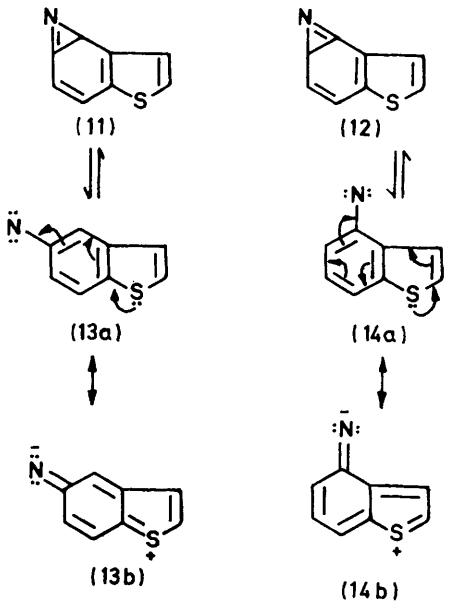
The formation of the diamines (6)—(9) can be rationalised as shown in the Scheme. The aziridine intermediate



SCHEME

which arises from a singlet nitrene may undergo ring-opening to give the products directly, or ring-expansion to give a thienoazepine which then contracts to give the diamine. The latter process is expected to be thermodynamically less favourable since it involves loss of aromaticity in both rings. Collapse of an azepine to an *o*-phenylenediamine has been observed previously.[9] Ring-contraction of azepines to give derivatives of *o*-phenylenediamine under acylation [8,10] or alkylation [11] conditions is well known. However, the formation of an *ortho*-diamine *during* the decomposition of an aryl azide seems not to have been reported. Formation of the diamines (6)—(9) is favoured by retention of aromaticity in both rings of the product. If a 1*H*-thienoazepine is formed as an intermediate, it may rearrange to the more stable 3*H*-thienoazepine. It is possible that formation of the thienoazepines is kinetically controlled whereas formation of the diamines (6)—(9) is thermodynamically controlled.[12] We hope to establish eventually which of the two proposed routes is responsible for the formation of these diamines. Their formation is good evidence that azirines are produced by decomposition of the starting azides.

We offer the following explanation for the contrasting behaviour of 4- and 5-azidobenzo[*b*]thiophen. An equilibrium exists between an aryl singlet nitrene and the corresponding azirine intermediate, as shown [(11) ⇌ (13) and (12) ⇌ (14)]. With a strong nucleophile the azirine will undergo an addition reaction or, failing this, it will revert to a singlet nitrene, which will eventually degenerate to a triplet state. In the case of the azirine (11) derived from 5-azidobenzo[*b*]thiophen, addition of a strong nucleophile is expected to be unimpeded but in the case of the azirine (12) derived from 4-azidobenzo[*b*]thiophen steric hindrance (*peri*-interaction) will make addition more difficult. Consequently, the azirine (12) is likely to revert to the singlet nitrene. Moreover, formation of the azirine (11) is favoured since it involves electrophilic attack in an 'α-position' (naphthalene nomenclature) whereas formation of the corresponding azirine (12) involves attack in a 'β-position.' The relative stabilities of the two singlet nitrenes (13) and (14) may be a further contributory factor. For the latter, mesomerism involves an *ortho*-quinonoid contributor (14b) whilst for the former it involves a *para*-quinonoid contributor (13b). Consequently, singlet benzo[*b*]thiophen-4-ylnitrene (14) is more likely to degenerate to a triplet state without

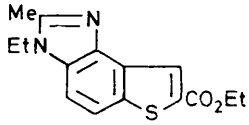


interception than benzo[*b*]thiophen-5-ylnitrene (13), which has more chance to react as shown in the Scheme.

The 4,5-diamines which can be made by our route are interesting compounds in their own right. Thus, we prepared ethyl 3-ethyl-2-methylthieno[3,2-*e*]benzimidazole-7-carboxylate (15) by treatment of the diamine (8) with formic acid–hydrogen peroxide.[13] Previously, 2-methyl-1*H*-thieno[3,2-*e*]benzimidazole (16) has been prepared by heating 5-acetamido-4-aminobenzo[*b*]thiophen under reduced pressure.[14] The parent system, 1*H*-thieno[3,2-*e*]benzimidazole, has been prepared from

[9] R. K. Smalley and H. Suschitzky, *J. Chem. Soc.*, 1964, 5922.
[10] W. von E. Doering and R. A. Odum, *Tetrahedron*, 1966, **22**, 81.
[11] F. R. Atherton and R. W. Lambert, *J.C.S. Perkin I*, 1973, 1079.
[12] R. A. Abramovitch, S. R. Challand, and E. F. V. Scriven, *J. Amer. Chem. Soc.*, 1972, **94**, 1374.
[13] O. Meth-Cohn and H. Suschitzky, *J. Chem. Soc.*, 1963, 4666.
[14] Z. I. Moskalenko, U.S.S.R. P. 230,826/1968 (*Chem. Abs.*, 1969, **70**, 87,815).

4,5-diaminobenzo[*b*]thiophen and formic acid.[15] Its 8-methyl derivative may be prepared similarly. 2-Methyl-1*H*-[1]benzothieno[2,3-*d*]imidazole (17), isomeric with (16), is also known.[16,17]



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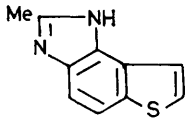

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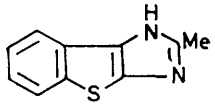

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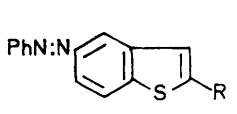
Photolysis of ethyl 5-azidobenzo[*b*]thiophen-2-carboxylate in a large excess of cyclohexylamine gave ethyl 5-aminobenzo[*b*]thiophen-2-carboxylate as the only isolable product (15% yield). A similar photolysis in aniline gave starting material (15% recovery), ethyl 5-phenylazobenzo[*b*]thiophen-2-carboxylate (see later) (18; R = CO_2Et) (9·5%), and tar. The use of triethylamine [10] as a diluent in these reactions resulted in a greater recovery of starting material.

In an attempt to extend our work to nucleophiles other than amines, we photolysed ethyl 5-azidobenzo[*b*]-thiophen-2-carboxylate in methanol, ethanol, and in a solution of benzenethiol in ether. In methanol, we obtained starting material (40% recovery), the azo-compound (19) (11% yield), and tar. A similar mixture of products was obtained in ethanol, whereas photolysis in the presence of benzenethiol gave ethyl 5-amino-benzo[*b*]thiophen-2-carboxylate (56% yield) and diphenyl disulphide (76% yield). In these reactions, therefore, the initially generated nitrene, 2-ethoxycarbonylbenzo[*b*]thiophen-5-ylnitrene, reacts mainly as a triplet and does not react as shown in the Scheme. Smolinsky [18] obtained aniline and diphenyl disulphide from photolysis of phenyl azide in benzenethiol and suggested the intermediacy of a triplet nitrene.

Thermolysis of 5-azidobenzo[*b*]thiophen in aniline gave 5-phenylazobenzo[*b*]thiophen (18; R = H) (15%) and azobenzene. Similar treatment of ethyl 5-azidobenzo-



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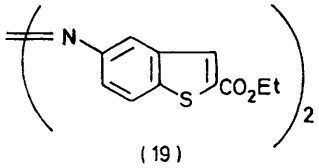

(19)

[*b*]thiophen-2-carboxylate gave ethyl 5-aminobenzo[*b*]-thiophen-2-carboxylate (20%) and a small amount of azobenzene. In hot piperidine this azide yielded ethyl 5-aminobenzo[*b*]thiophen-2-carboxylate (11%) and starting material (20% recovery). The formation of the mixed azo-compounds (18; R = H or CO_2Et) is interesting since only isolated examples have been prepared in this way previously.[19]

EXPERIMENTAL

The spectroscopic instruments used were the same as those reported in the preceding paper.[1] All new compounds gave mass spectra consistent with the proposed structures. Azides were photolysed with a high pressure mercury vapour lamp (type Q81 Quartzlampen GmbH, Hanau) through a Pyrex filter. Light petroleum refers to the fraction of b.p. 60—80° unless stated otherwise. Azidobenzo[*b*]thiophens were prepared as described in the preceding paper.[1] Yields quoted are based on starting material consumed.

Photolysis of 4-*Azidobenzo*[b]*thiophen in Diethylamine.*—A solution of the azide (1·0 g, 5·7 mmol) in diethylamine (100 ml) was irradiated for 18 h at room temperature. The excess of diethylamine was distilled off under reduced pressure, and the product was chromatographed on alumina. Light petroleum–ether (10 : 1) eluted starting material (0·4 g, 40% recovery) and 4,4′-*azobenzo*[b]*thiophen* (5) (0·1 g, 20% based on starting material consumed), m.p. 164—165° (from benzene) (Found: C, 65·1; H, 3·3; N, 9·3. $C_{16}H_{10}N_2S_2$ requires C, 65·3; H, 3·4; N, 9·5%). Ether eluted 4-aminobenzo[*b*]thiophen (0·3 g, 59%), m.p. 51—52°, identical with an authentic sample,[1] a trace of a compound which was not investigated, and tar.

Photolysis of 5-*Azidobenzo*[b]*thiophen.*—(a) *In diethylamine.* A solution of the azide (0·5 g, 5·7 mmol) in diethylamine (50 ml) was irradiated for 18 h at room temperature. The excess of diethylamine was distilled off, and the residue was chromatographed on silica. Light petroleum–ether (4 : 1) eluted 4-*amino*-5-*diethylaminobenzo*[b]*thiophen* (6) (0·15 g, 24%), b.p. 104—108° at 0·2 mmHg, $\nu_{max.}$ (Nujol) 3345 and 3445 cm^{-1} (NH_2), τ (C_6D_6) 2·65—3·15 (4H, m, aromatic), 6·00br (2H, s, exchangeable, NH_2), 7·22 (4H, q, *J* 7·0 Hz, CH_2), and 9·09 (6H, t, *J* 7·0 Hz, CH_3) (Found: C, 65·1; H, 7·0; N, 12·5. $C_{12}H_{16}N_2S$ requires C, 65·4; H, 7·3; N, 12·7%); the *diacetyl derivative* (25%) had m.p. 98—100° (from ethanol), $\nu_{max.}$ (Nujol) 1700 cm^{-1} (C:O), τ ($CDCl_3$) 2·11 and 2·76 (2H, d, aromatic, *J* 9·0 Hz, 6-H and 7-H), 2·48 and 2·98 (2H, d, aromatic, *J* 6·0 Hz, 2-H and 3-H) (precise assignments not made), 6·95 (4H, q, *J* 7·0 Hz, CH_2), 8·94 (6H, t, *J* 7·0 Hz, CH_3), and 7·68 (6H, s, acetyl CH_3) (Found: C, 63·25; H, 6·8; N, 9·4. $C_{16}H_{20}N_2O_2S$ requires C, 63·1; H, 6·6; N, 9·2%).

(b) *In morpholine.* A solution of the azide (1·0 g, 5·7 mmol) in morpholine (100 ml) was treated as described in (a). The product was chromatographed on silica. Light petroleum eluted starting material (25% recovery); light petroleum–ether (1 : 1) eluted 4-*amino*-5-*morpholinobenzo*-[b]*thiophen* (7) (0·4 g, 40% based on starting material consumed), m.p. 151—152° (from ethanol), $\nu_{max.}$ (Nujol) 3345 and 3430 cm^{-1} (NH_2), τ ($CDCl_3$) 2·55—2·90 (4H, m, aromatic), 5·50br (2H, s, exchangeable, NH_2), 6·00—6·20 (4H, m, OCH_2), and 6·95—7·15 (4H, m, NCH_2) (Found: C,

[15] N. B. Chapman, K. Clarke, and K. S. Sharma, *J. Chem. Soc.* (*C*), 1971, 919.
[16] V. G. Zhiryakov and P. I. Abramenko, U.S.S.R. P. 224,524/1968 (*Chem. Abs.*, 1969, **70**, 20,060); P. I. Abramenko, *Khim. geterotsikl. Soedinenii*, 1970, 1473 (*Chem. Abs.*, 1971, **74**, 53,653).
[17] M. S. El Shanta, R. M. Scrowston, and M. V. Twigg, *J. Chem. Soc.* (*C*), 1967, 2364.
[18] G. Smolinsky, *J. Org. Chem.*, 1961, **26**, 4108.
[19] E. F. V. Scriven, H. Suschitzky, and G. V. Garner, *Tetrahedron Letters*, 1973, 103.

61·3; H, 5·9; N, 11·8. $C_{12}H_{14}N_2OS$ requires C, 61·5; H, 6·0; N, 11·95%).

Photolysis of Ethyl 5-Azidobenzo[b]*thiophen-2-carboxylate.*—(a) *In diethylamine.* A stirred suspension of the azide (1·0 g, 4·0 mmol) in diethylamine (100 ml) was irradiated for 24 h. The excess of diethylamine was distilled off under reduced pressure, and the residue was chromatographed on alumina. Light petroleum–ether (4 : 1) eluted starting material (25% recovery); a 2 : 1 ratio of the same solvent system eluted *ethyl 4-amino-5-diethylaminobenzo*[b]*thiophen-2-carboxylate* (8) (0·5 g, 57% based on starting material consumed), m.p. 73—74° (from ethanol), $\nu_{max.}$ (Nujol) 3365 and 3470 (NH_2) and 1710 cm^{-1} (C:O), τ ($CDCl_3$) 1·87 (1H, s, 3-H), 2·73 (2H, appeared as a singlet, 6-H and 7-H), 5·30br (2H, s, exchangeable, NH_2), 5·58 (2H, q, J 7·0 Hz, ester CH_2), 7·02 (4H, q, J 7·0 Hz, CH_2), 8·60 (3H, t, J 7·0 Hz, ester CH_3), and 9·01 (6H, t, J 7·0 Hz, CH_3) (Found: C, 61·7; H, 6·9; N, 9·5. $C_{15}H_{20}N_2O_2S$ requires C, 61·6; H, 6·9; N, 9·6%); the *diacetyl derivative* (47%) had m.p. 100—102° (from ethanol), $\nu_{max.}$ (Nujol) 1695 (acetyl C:O) and 1725 cm^{-1} (ester C:O), τ ($CDCl_3$) 2·15 and 2·65 (2H, d, aromatic, 6-H and 7-H, $J_{6,7}$ 9·0 Hz) (precise assignments not made), 2·28 (1H, s, 3-H), 5·57 (2H, q, J 7·0 Hz, ester CH_2), 6·95 (4H, q, J 7·0 Hz, CH_2), 7·68 (6H, s, acetyl CH_3), 8·60 (3H, t, J 7·0 Hz, ester CH_3), and 8·96 (6H, t, J 7·0 Hz, CH_3) (Found: C, 60·0; H, 6·3; N, 7·5. $C_{19}H_{24}N_2O_4S$ requires C, 60·6; H, 6·4; N, 7·4%).

(b) *In piperidine.* A 1% solution of the azide in piperidine was irradiated for 48 h and then treated as described in (a). The product was chromatographed on alumina. Light petroleum–ether (4 : 1) eluted starting material (45% recovery); a 1 : 1 ratio of the same solvents eluted *ethyl 4-amino-5-piperidinobenzo*[b]*thiophen-2-carboxylate* (9) (24%), m.p. 115—116° (from ethanol), $\nu_{max.}$ (Nujol) 3360 and 3455 (NH_2), and 1712 cm^{-1} (C:O), τ ($CDCl_3$) 1·89 (1H, s, 3-H), 2·74 (2H, appeared as a singlet, 6-H and 7-H), 5·40br (2H, s, exchangeable, NH_2), 5·57 (2H, q, J 7·0 Hz, ester CH_2), 8·60 (3H, t, J 7·0 Hz, CH_3), 7·15br (4H, m, α-CH_2), and 8·35br (6H, m, β- and γ-CH_2) (Found: C, 62·95; H, 6·65; N, 9·0. $C_{16}H_{20}N_2O_2S$ requires C, 63·1; H, 6·6; N, 9·2%).

(c) *In cyclohexylamine.* (i) A 1% solution of the azide in cyclohexylamine was irradiated for 48 h. The product was chromatographed on silica gel. Light petroleum–ether (3 : 1) eluted ethyl 5-aminobenzo[*b*]thiophen-2-carboxylate (15%), b.p. 160—165° at 0·5 mmHg, identical with an authentic sample.[1]

(ii) A solution of the azide (1·0 g, 4·0 mmol) and cyclohexylamine (1 ml) in triethylamine (100 ml) was irradiated for 48 h. Concentration of the mixture to 2 ml followed by filtration gave starting material (80% recovery).

(d) *In aniline.* (i) A solution of the azide (1·0 g, 4·0 mmol) in aniline (160 ml) was irradiated for 24 h. The excess of aniline was distilled off and the product was chromatographed on alumina. Light petroleum–ether (10 : 1) eluted starting material (15% recovery) and *ethyl 5-phenylazobenzo*[b]*thiophen-2-carboxylate* (18; R = CO_2Et) (0·1 g, 9·5% based on starting material consumed), b.p. 160—165° at 0·4 mmHg, $\nu_{max.}$ (Nujol) 1712 cm^{-1} (C:O), τ ($CDCl_3$) 1·55—2·60 (9H, m, aromatic), 5·60 (2H, q, J 7·0 Hz, CH_2), and 8·60 (3H, q, J 7·0 Hz, CH_3) (Found: C, 65·7; H, 4·3; N, 8·9. $C_{17}H_{14}N_2O_2S$ requires C, 65·8; H, 4·5; N, 9·0%).

(ii) A solution of the azide (1·0 g) and aniline (1·0 ml) in triethylamine (100 ml) was irradiated for 24 h. After removal of the amines the product was chromatographed on alumina; light petroleum–ether (4 : 1) eluted starting material (70% recovery).

(e) *In methanol.* A solution of the azide (1·0 g, 4·0 mmol) in methanol (100 ml) was treated as described in (a). The product was chromatographed on alumina; light petroleum–ether (3 : 2) eluted starting material (0·4 g, 40% recovery). Ether eluted *diethyl 4,4′-azobenzo*[b]*thiophen-2-carboxylate* (19) (0·05 g, 11%), m.p. 192—193° (from benzene), $\nu_{max.}$ (Nujol) 1715 cm^{-1} (C:O) (Found: C, 60·0; H, 4·0; N, 6·2. $C_{22}H_{18}N_2O_4S_2$ requires C, 60·25; H, 4·1; N, 6·4%).

(f) *In ethanol.* A 1% solution of the azide in ethanol was treated as described in (a). Work-up in the usual way gave starting material (40% recovery) and the azo-compound (19) (8%).

(g) *In the presence of benzenethiol.* A solution of the azide (1·0 g, 4·0 mmol) and benzenethiol (1·0 ml) in ether (100 ml) was irradiated for 48 h. The resulting mixture was washed successively with 4N-sodium hydroxide and water, and dried ($MgSO_4$). The solvent was distilled off and the product chromatographed on alumina. Light petroleum–ether (4 : 1) eluted diphenyl disulphide (0·8 g, 76%), m.p. 55—57°, identical with an authentic sample; a 3 : 2 ratio of the same solvents eluted ethyl 5-aminobenzo[*b*]thiophen-2-carboxylate (0·5 g, 56%), m.p. 92—94° (from ethanol), identical in all other respects with an authentic sample.[1]

Thermolysis of 5-Azidobenzo[b]*thiophen in Aniline.*—A solution of the azide (0·5 g, 2·86 mmol) in aniline (50 ml) was heated at 170° for 1 h. The excess of aniline was distilled off and the residue was chromatographed on alumina. Light petroleum effected a partial separation of the components and eluted azobenzene (0·1 g), identical with an authentic sample, and *5-phenylazobenzo*[b]*thiophen* (18; R = H) (0·1 g, 15%), m.p. 107—108° (from light petroleum), τ ($CDCl_3$) 1·45—2·50 (m, aromatic) (Found: C, 70·3; H, 4·1; N, 11·6. $C_{14}H_{10}N_2S$ requires C, 70·4; H, 4·2; N, 11·8%).

Thermolysis of Ethyl 5-Azidobenzo[b]*thiophen-2-carboxylate.*—(a) *In aniline.* A solution of the azide (1·0 g, 4·0 mmol) in aniline (50 ml) was heated under reflux for 20 h and the product was chromatographed on alumina after the excess of aniline had been distilled off. Light petroleum–ether (4 : 1) eluted azobenzene (0·1 g), and ether eluted ethyl 5-aminobenzo[*b*]thiophen-2-carboxylate [1] (0·18 g, 20%), identical with an authentic sample.

(b) *In piperidine.* A solution of the azide (0·5 g, 2·0 mmol) in piperidine (50 ml) was heated under reflux for 20 h. The excess of piperidine was distilled off and the product was chromatographed on alumina. Light petroleum–benzene (1 : 1) eluted starting material (0·05 g, 10% recovery). Ethyl acetate eluted ethyl 5-aminobenzo[*b*]thiophen-2-carboxylate (0·05 g, 11%), identical with an authentic sample.[1]

Deamination of Ethyl 4-Amino-5-diethylaminobenzo[b]*thiophen-2-carboxylate.*—A solution of sodium nitrite (0·31 g) in water (5 ml) was added to a stirred suspension of the amine (1·0 g, 3·4 mmol) in a mixture of concentrated hydrochloric acid (3 ml) and water (3 ml) at 0°. The resulting solution was filtered into 30% hypophosphorous acid (100 ml) at 0° and the mixture was kept at 0° for 48 h. It was then made alkaline with 2N-sodium hydroxide; extraction with chloroform gave *ethyl 5-diethylaminobenzo*[b]*thiophen-2-carboxylate* (0·1 g, 10%), b.p. 125—128° at 0·4 mmHg

(Kugelrohr apparatus), $\nu_{max.}$ (film) 1715 cm^{-1} (C:O), τ (CCl_4) 2·15 (m, 3-H and 7-H), 2·50 (q, $J_{4,6}$ 2·0, $J_{4,7}$ < 1·0 Hz, 4-H), 3·05 (q, $J_{4,6}$ 2·0, $J_{6,7}$ 10·0 Hz, 6-H), 5·69 (2H, q, J 7·0 Hz, ester CH_2), 6·66 (4H, q, J 6·5 Hz, CH_2), 8·66 (3H, t, J 7·0 Hz, ester CH_3), and 8·90 (6H, t, J 6·5 Hz, CH_3) (Found: C, 64·8; H, 6·7; N, 4·8. $C_{15}H_{19}NO_2S$ requires C, 65·0; H, 6·9; N, 5·05%).

Ethyl 5-Acetamidobenzo[b]*thiophen-2-carboxylate*.—A mixture of ethyl 5-aminobenzo[*b*]thiophen-2-carboxylate [1] (30·0 g, 135·0 mmol) and acetic anhydride (500 ml) was heated under reflux for 2 h, cooled, and poured into water. The *product* (34·2 g, 96%) was filtered off; m.p. 175—177° (from ethanol), $\nu_{max.}$ (Nujol) 1655 (amide C:O), 1710 (ester C:O), and 3295 cm^{-1} (NH) (Found: C, 59·0; H, 5·2; N, 5·05. $C_{13}H_{13}NO_3S$ requires C, 59·3; H, 5·0; N, 5·3%).

Ethyl 5-Acetamido-4-nitrobenzo[b]*thiophen-2-carboxylate*.—A mixture of ethyl 5-acetamidobenzo[*b*]thiophen-2-carboxylate (4·0 g, 15·2 mmol), concentrated nitric acid (5 ml), and acetic acid (125 ml) was heated under reflux for 30 min, cooled, and poured into water. The *product* (4·4 g, 94%) was filtered off; m.p. 135—136° (from ethanol), $\nu_{max.}$ (Nujol) 1710 (amide C:O), 1730 (ester C:O), and 3375 cm^{-1} (NH), τ ($CF_3{\cdot}CO_2D$) 1·35 (1H, s, 3-H), 1·51 and 1·76 (2H, d, 6-H and 7-H, $J_{6,7}$ 9·0 Hz) (precise assignments not made), 5·34 (2H, q, J 7·0 Hz, CH_2), 8·44 (3H, t, J 7·0 Hz, CH_3), and 7·50 (3H, s, amide CH_3) (Found: C, 50·4; H, 4·0; N, 9·4. $C_{13}H_{12}N_2O_5S$ requires C, 50·6; H, 3·9; N, 9·1%).

Ethyl 5-Amino-4-nitrobenzo[b]*thiophen-2-carboxylate*.—A 1% solution of sodium hydroxide (80 ml) was added to a solution of the product (12·0 g, 39·0 mmol) from the previous reaction in ethanol (400 ml) and the resulting mixture was heated under reflux for 30 min, cooled, treated with charcoal, and filtered. Distillation left the *product* (9·8 g, 94%), m.p. 146—147° (from ethanol), $\nu_{max.}$ (Nujol) 1712 (C:O) and 3320 and 3425 cm^{-1} (NH_2), τ [$CDCl_3$–$(CD_3)_2SO$] 1·21 (1H, s, 3-H), 2·22 and 2·81 (2H, d, 6-H and 7-H, $J_{6,7}$ 10·0 Hz) (precise assignments not made), 5·57 (2H, q, J 7·0 Hz, CH_2), and 8·55 (3H, t, J 7·0 Hz, CH_3) (Found: C, 49·5; H, 3·8; N, 10·4. $C_{11}H_{10}N_2O_4S$ requires C, 49·6; H, 3·8; N, 10·5%).

Alkylation of Ethyl 5-Amino-4-nitrobenzo[b]*thiophen-2-carboxylate*.—A mixture of the amine (1·82 g, 6·8 mmol), ethyl iodide (2·2 g, 14·0 mmol), sodium hydroxide (0·55 g), and water (0·55 ml) was heated at 120° in a sealed tube for 16 h. The product was extracted with chloroform and chromatographed on alumina. Ether eluted *ethyl 5-ethylamino-4-nitrobenzo*[b]*thiophen-2-carboxylate* (10) (0·1 g, 8%), m.p. 146—147° (from ethanol), $\nu_{max.}$ (Nujol) 1710 (C:O) and 3320 cm^{-1} (NH), τ ($CDCl_3$) 1·00br (1H, s, exchangeable, NH), 1·09 (1H, s, 3-H), 2·16 and 2·94 (2H, d, 6-H and 7-H, $J_{6,7}$ 10·0 Hz) (precise assignments not made), 5·51 (2H, q, J 7·0 Hz, ester CH_2), 6·51 (2H, appeared as a quintet due to incompletely resolved coupling with NH proton, J 6·0 Hz, amine CH_2), and 8·57 (6H, t, J 7·0 Hz, 2 × Me) (Found: C, 53·0; H, 4·7; N, 9·7. $C_{13}H_{14}N_2O_4S$ requires C, 53·05; H, 4·8; N, 9·5%). Chloroform eluted starting material (30% recovery).

Ethyl 3-Ethyl-2-methylthieno[3,2-e]*benzimidazole-7-carboxylate* (15).—A mixture of ethyl 4-amino-5-diethylaminobenzo[*b*]thiophen-2-carboxylate (0·5 g, 1·7 mmol), formic acid (3 ml), and 30% hydrogen peroxide (1·5 ml) was heated on a steam-bath for 15 min. The mixture was diluted with water (10 ml) and neutralised with 2N-ammonium hydroxide. Extraction with chloroform gave the *product* (15) (0·15 g, 31%), b.p. 160—165° at 0·2 mmHg, m.p. 117—120°, $\nu_{max.}$ (Nujol) 1712 cm^{-1} (C:O), τ ($CDCl_3$) 1·28 (1H, s, 8-H), 2·41 and 2·62 (2H, d, 4-H and 5-H, $J_{4,5}$ 7·0 Hz) (precise assignments not made), 5·66 (2H, q, J 7·0 Hz, CH_2), 5·78 (2H, q, J 7·0 Hz, CH_2), 7·35 (3H, s, 2-CH_3), 8·60 (3H, t, J 7·0 Hz, CH_3), and 8·62 (3H, t, J 7·0 Hz, CH_3) (Found: C, 62·5; H, 6·05; N, 9·4. $C_{15}H_{16}N_2O_2S$ requires C, 62·5; H, 5·6; N, 9·7%).

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